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# *"High energy x-ray glass diffraction at high pressure & temperature"*

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ASU

# *Order within Disorder*

**Talk Outline**

- History and current beamlines
- Structure factors and Distribution functions
- Simulation – RMC, EPSR and MD
- High pressure :

  Amorphous ice, $GeSe_2$, $BeF_2$, $SiO_2$

- High temperature : Aerodynamic levitaton

  Forsterite glass, liquid $SiO_2$, alumino-silicates, $CaSiO_3$

A formation of skydivers illustrates order on an intermediate length scale.

P.S. Salmon *Nature Materials* 1, 87–88 (2002)

# A brief history

*"**X-Ray Determination of Structure of Glass**"*
*B. E. Warren J. Am. Ceram. Soc. 17 (1934) 249.*

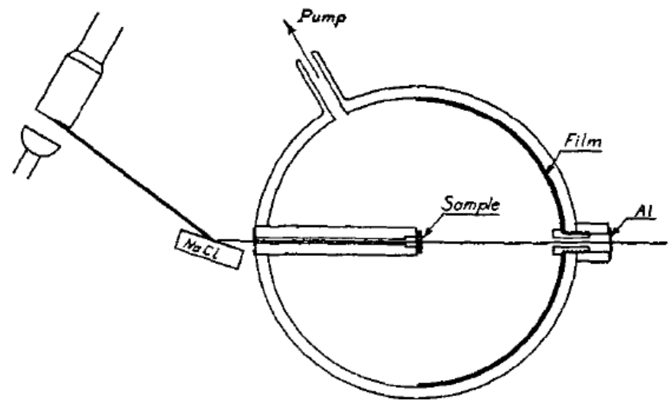



FIG. 1.—Vacuum camera with monochromator for making X-ray diffraction patterns of glass.

*Gamma Ray diffraction :*
*"**New experimental studies of the structure of fluids**"*
*P.A. Egelstaff, Adv. Chem. Phys. 53 (1983) 1.*

*Synchrotron radiation :*
*"**Amorphous silica studied by high energy X-ray diffraction** " H.F. Poulsen, J. Neuefeind, H.-B. Neumann, J.R. Schneider and M.D. Zeidler, J. Non-Cryst. Sol. 188 (1995) 63.*

*"**Effects of very high pressures on Glass**"*
*P.W. Bridgman and I. Simon*
*J. Applied Physics 24 (1953) 405.*

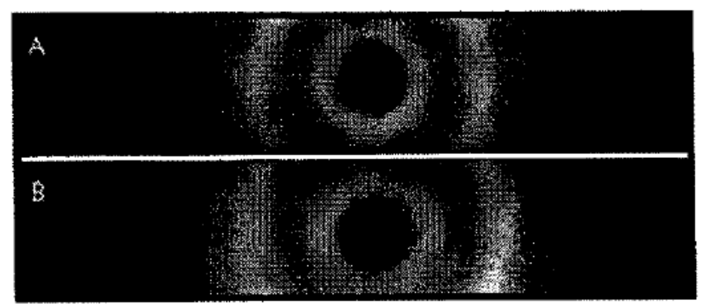
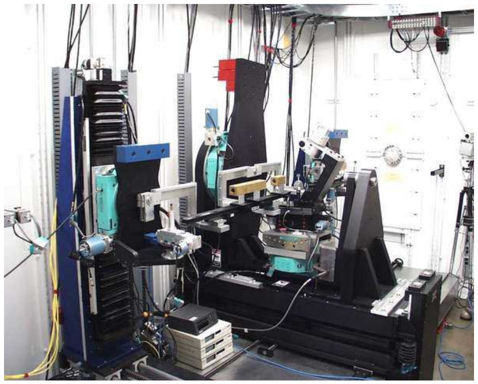
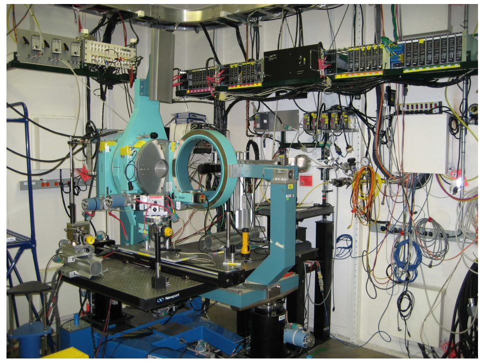


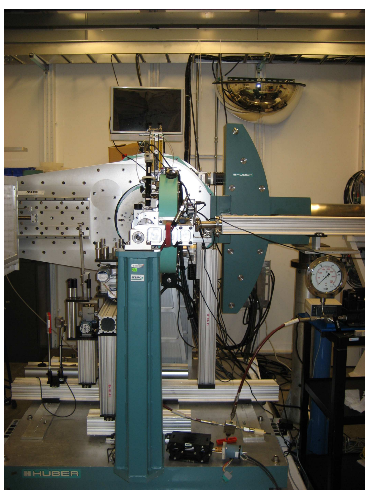

FIG. 9. X-ray diffraction patterns of vitreous silica before compression (A) and after compression to density 17.5 percent

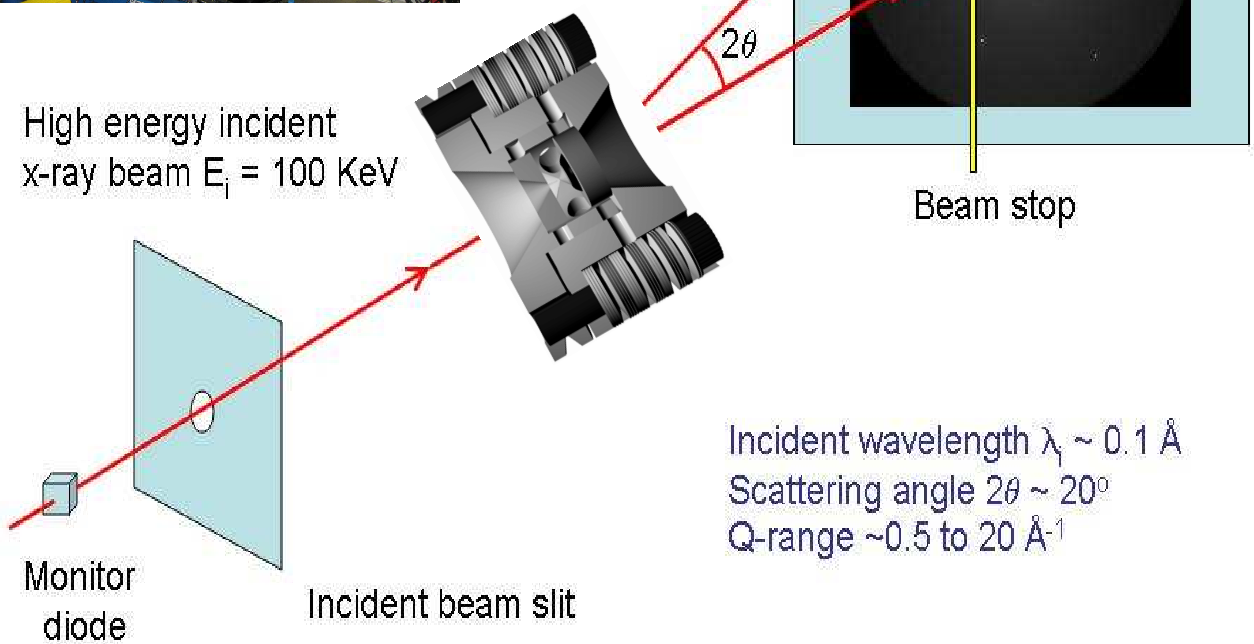
*"**X-ray diffraction from levitated liquids**"*
*S. Krishnan and D.L. Price*
*J. Phys.: Condens. Matter 12 (2000) R145.*

# *Some high energy x-ray beamlines at APS*





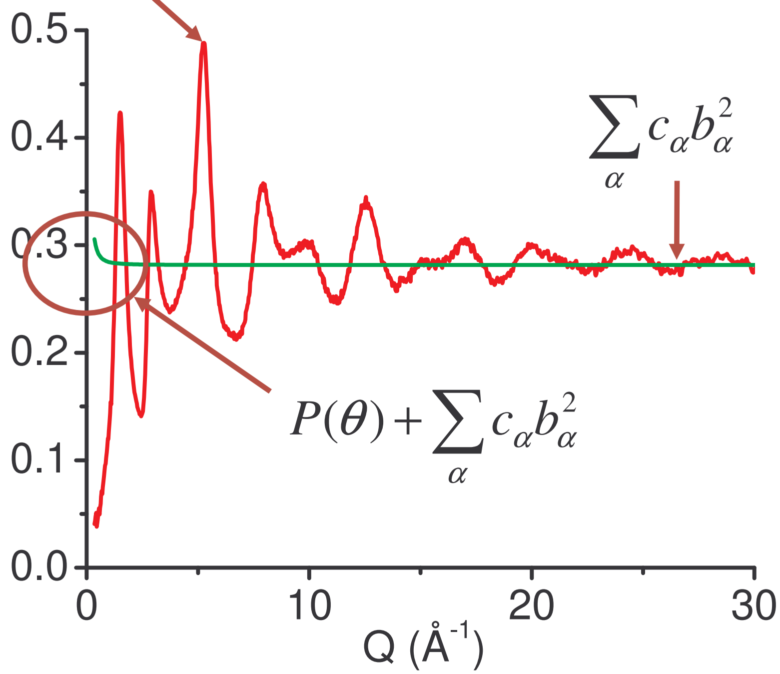




# *Total scattering*

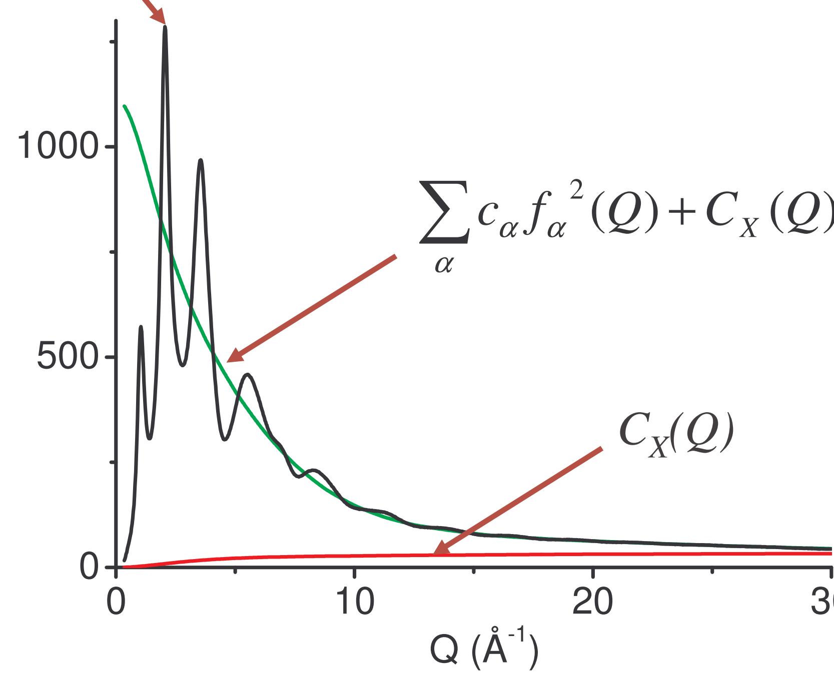
## Neutron

$$\frac{d\sigma_N}{d\Omega} = \sum_\alpha c_\alpha b_\alpha^2 + P(\theta) + F_N(Q)$$

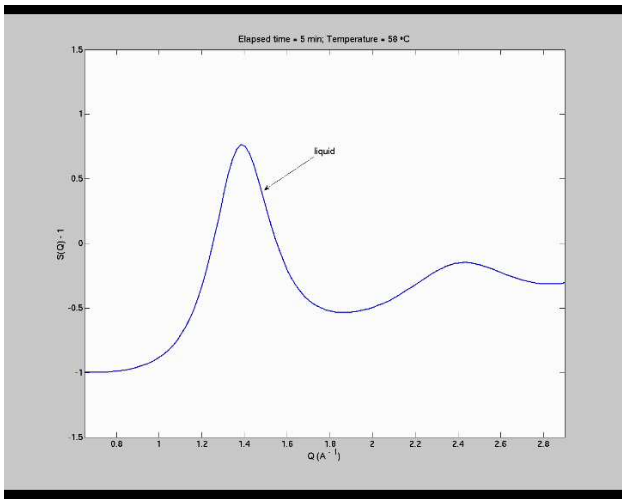



## X-ray

$$\frac{d\sigma_X}{d\Omega} = \sum_\alpha c_\alpha f_\alpha^{\ 2}(Q) + C_X(Q) + I_X(Q)$$

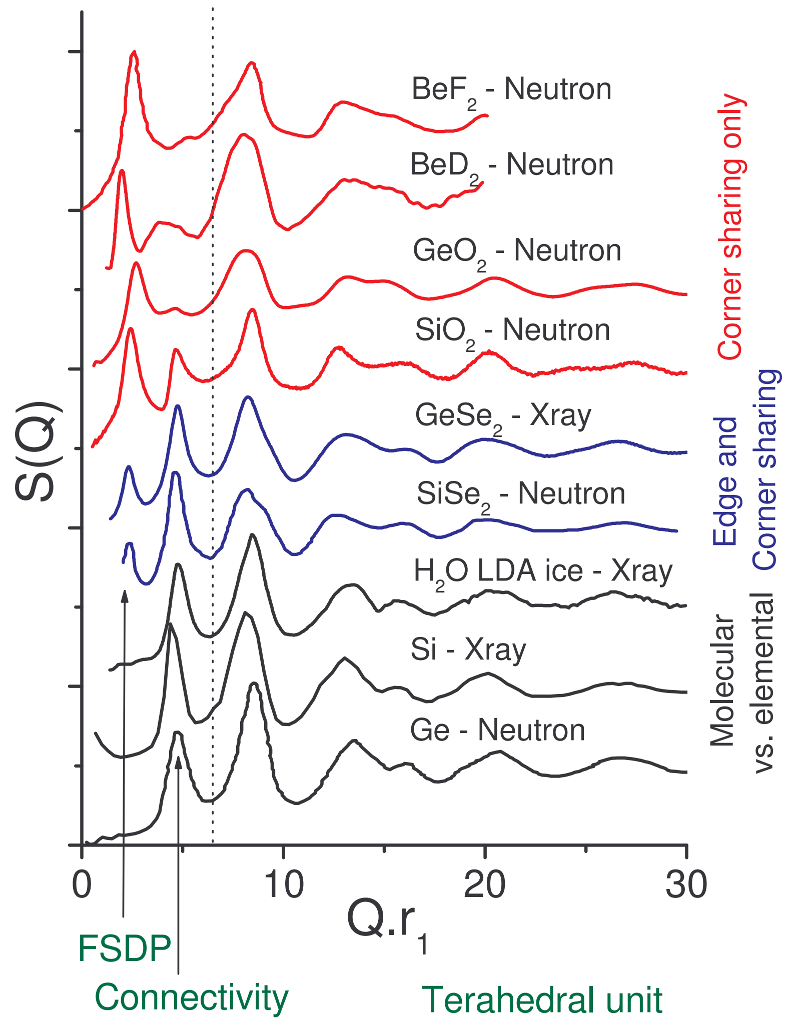


# *Network Glasses*




*Intermediate range chemical ordering in amorphous and liquid water, Si and Ge.*
C.J. Benmore *et al.* PRB 72 (2005) 132201.

*Compositional changes of the first sharp diffraction peak in binary selenide glasses*
E. Bychkov, C.J. Benmore, and D.L. Price
PRB 72 (2005) 172107.



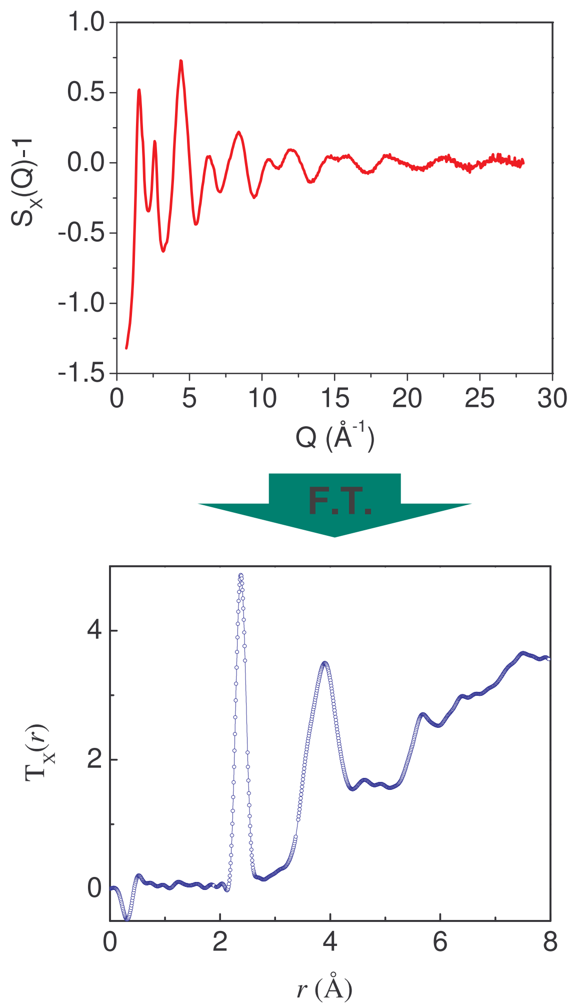
# *Distribution functions*

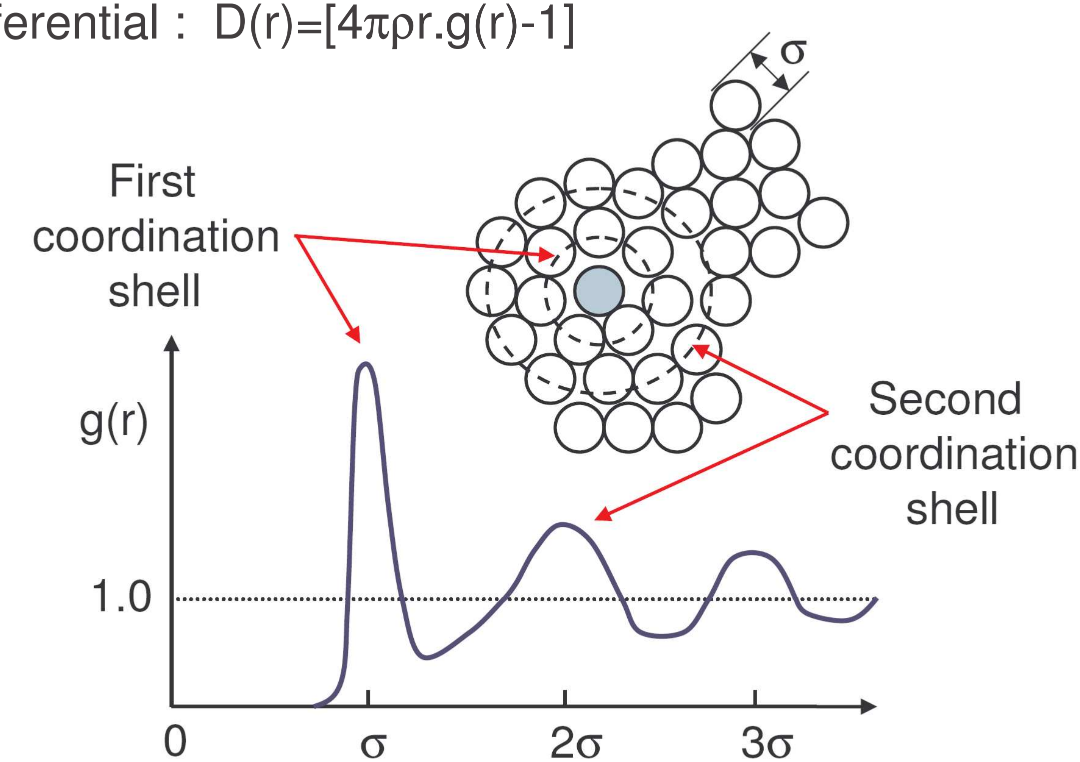
$$g(r) = 1 + \frac{1}{2\pi^2 \rho r} \int Q\, i(Q) M(Q) \sin(Qr)\, dQ$$

Fourier Transformation

Total : T(r)=4πρr.g(r)

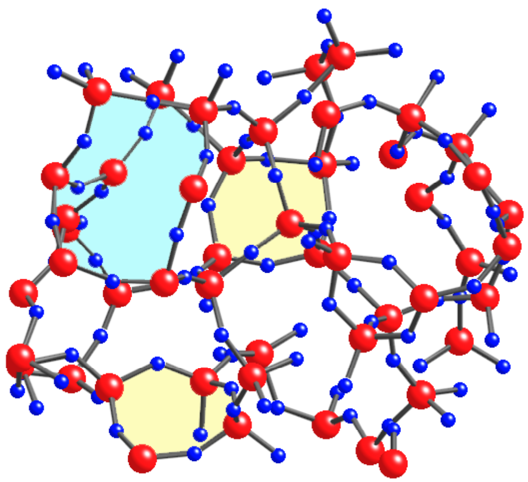
Differential : D(r)=[4πρr.g(r)-1]



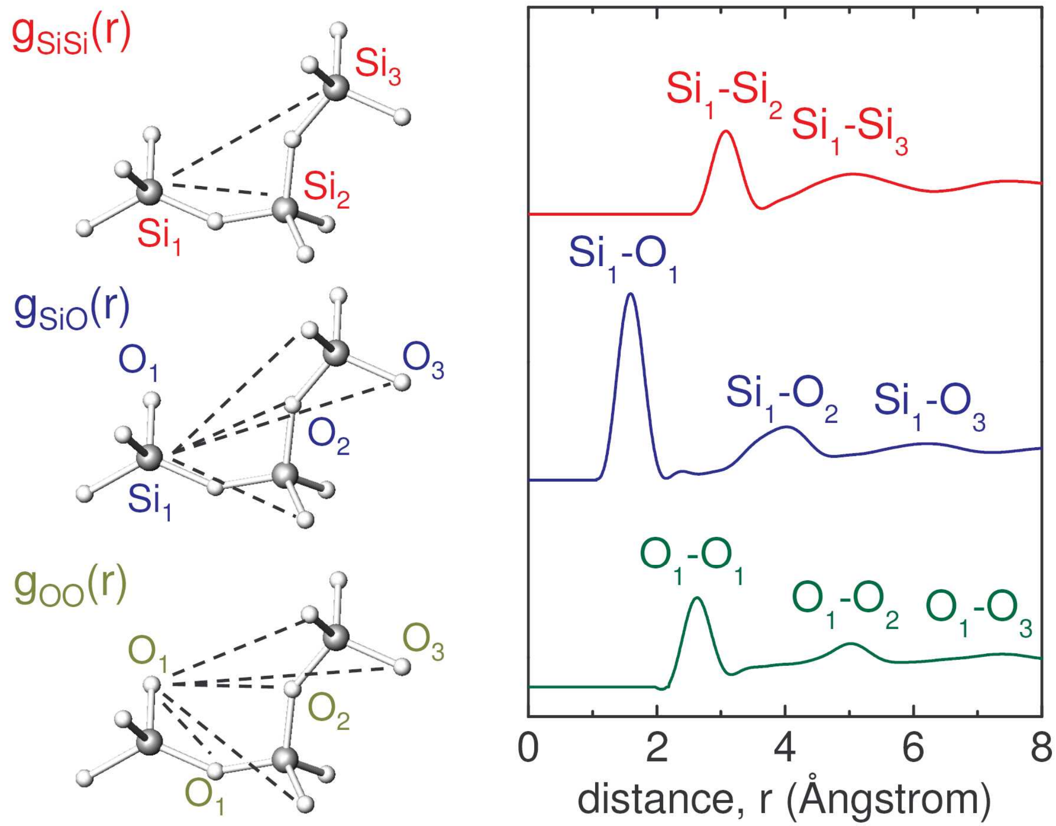



# Partial Pair Distribution Functions

- Vitreous Silica



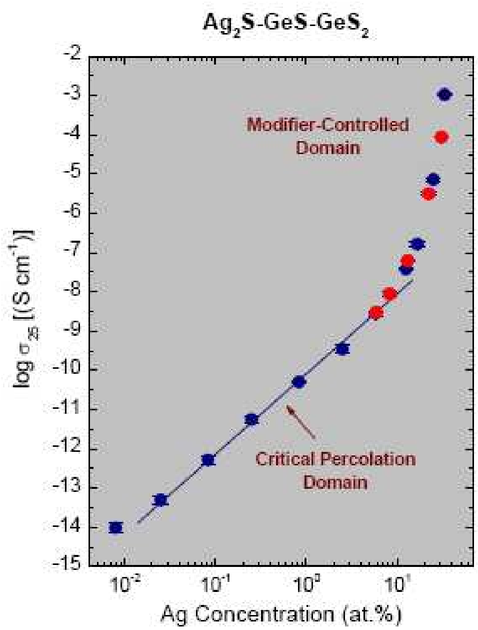
Courtesy of Shinji Kohara




*Intermediate range order in vitreous silica from a partial structure factor analysis.*
Q. Mei, C.J. Benmore, S. Sen, R. Sharma and J.L. Yarger. .PRB 78 (2008) 144204.

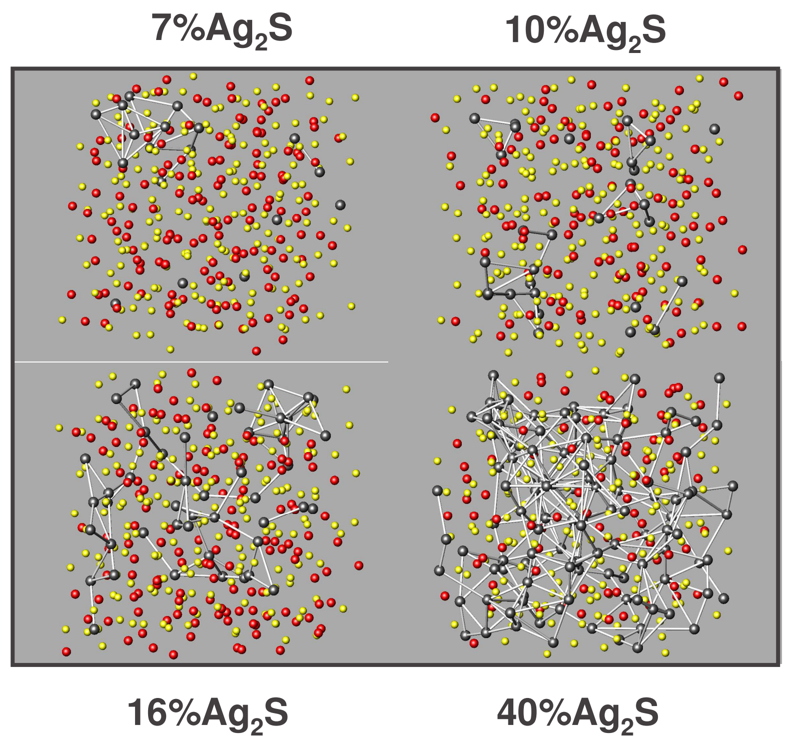
# *Reverse Monte Carlo Simulation*

- Fast ion conducting glasses




- Ionic conductivity increases by 10 orders of magnitude with increasing Ag content from 30 ppm to 35 at.%.

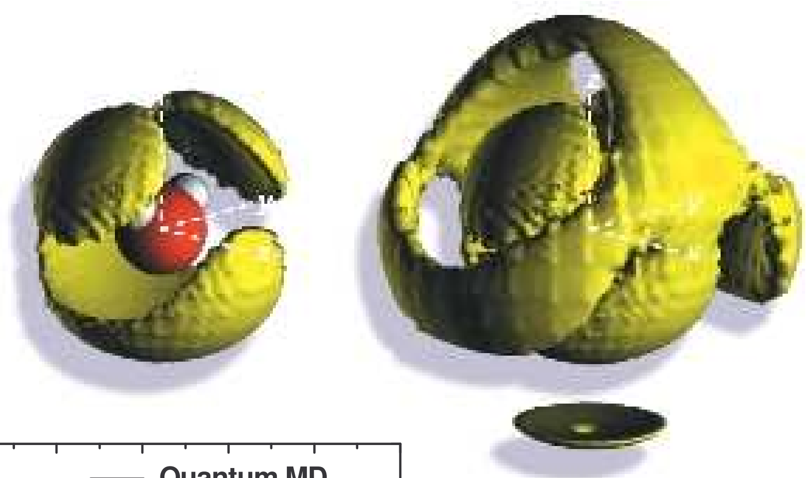
**Ge: Red S: Yellow Ag: Silver**

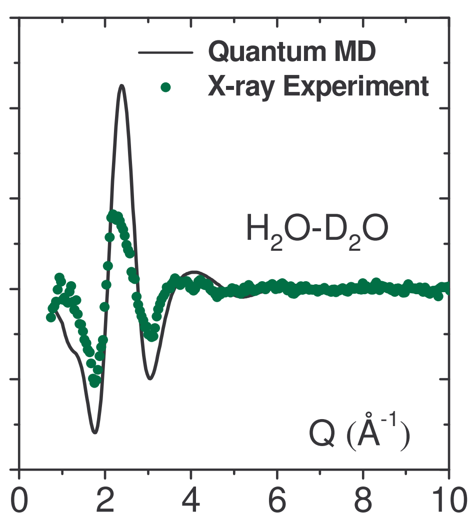


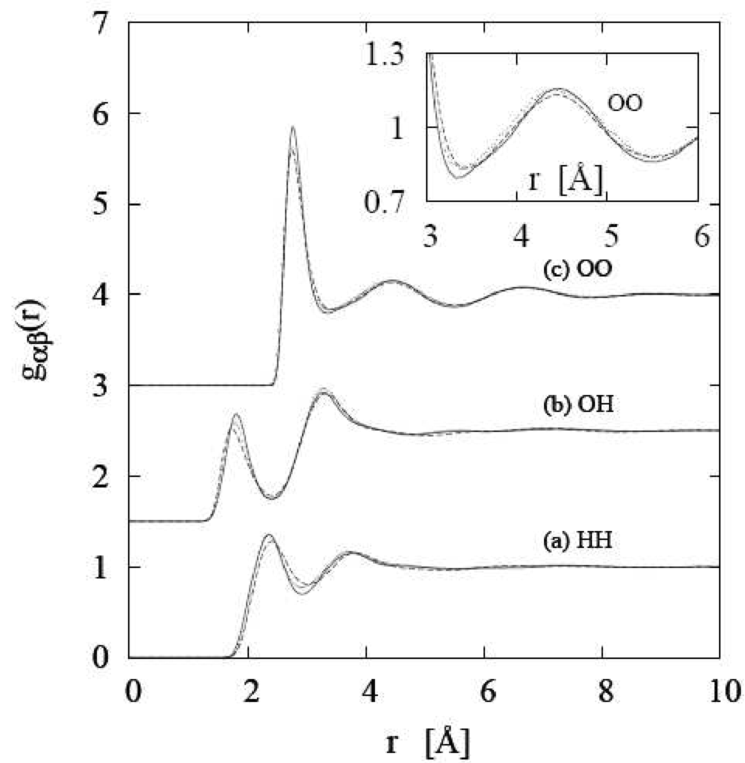

*Silver-silver correlations in AgGeS glasses*
E. Bychkov et al. *Proc. 9th Intern. Conf. on the Structure of Non-Crystalline Solids* (2004), 80

# *Empirical Potential Structure Refinement*

- Quantum isotope effects in water



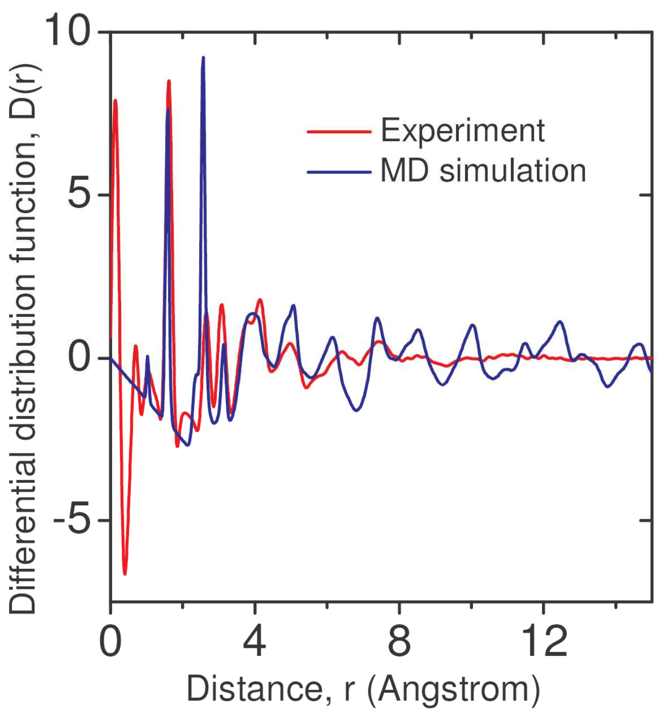


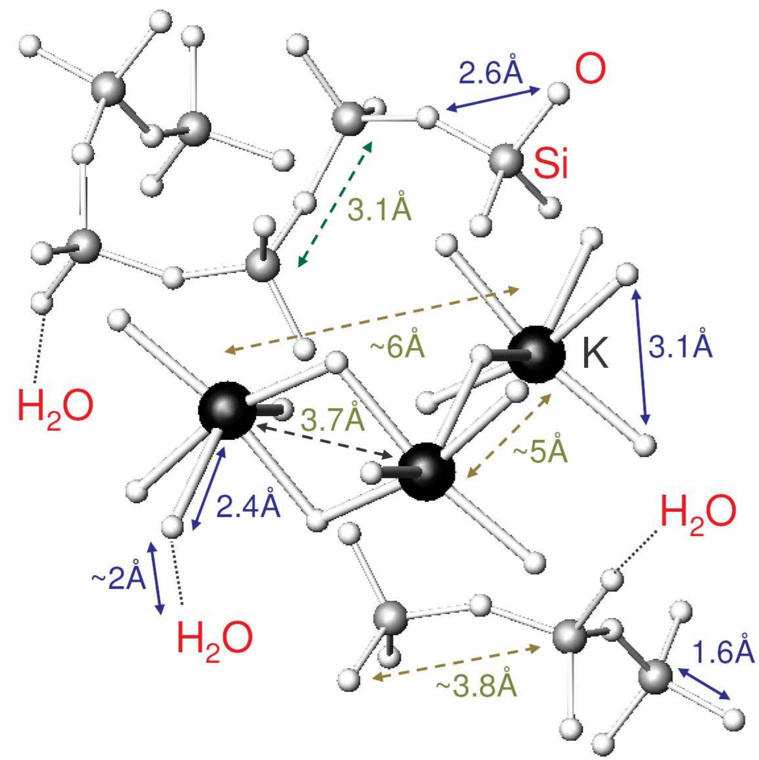




*Quantum differences between light and heavy water*
A.K. Soper and C.J. Benmore
PRL 101 (2008) 065502.

# *Molecular dynamics*

- How alkali-silicate gels crack large concrete dams and bridges

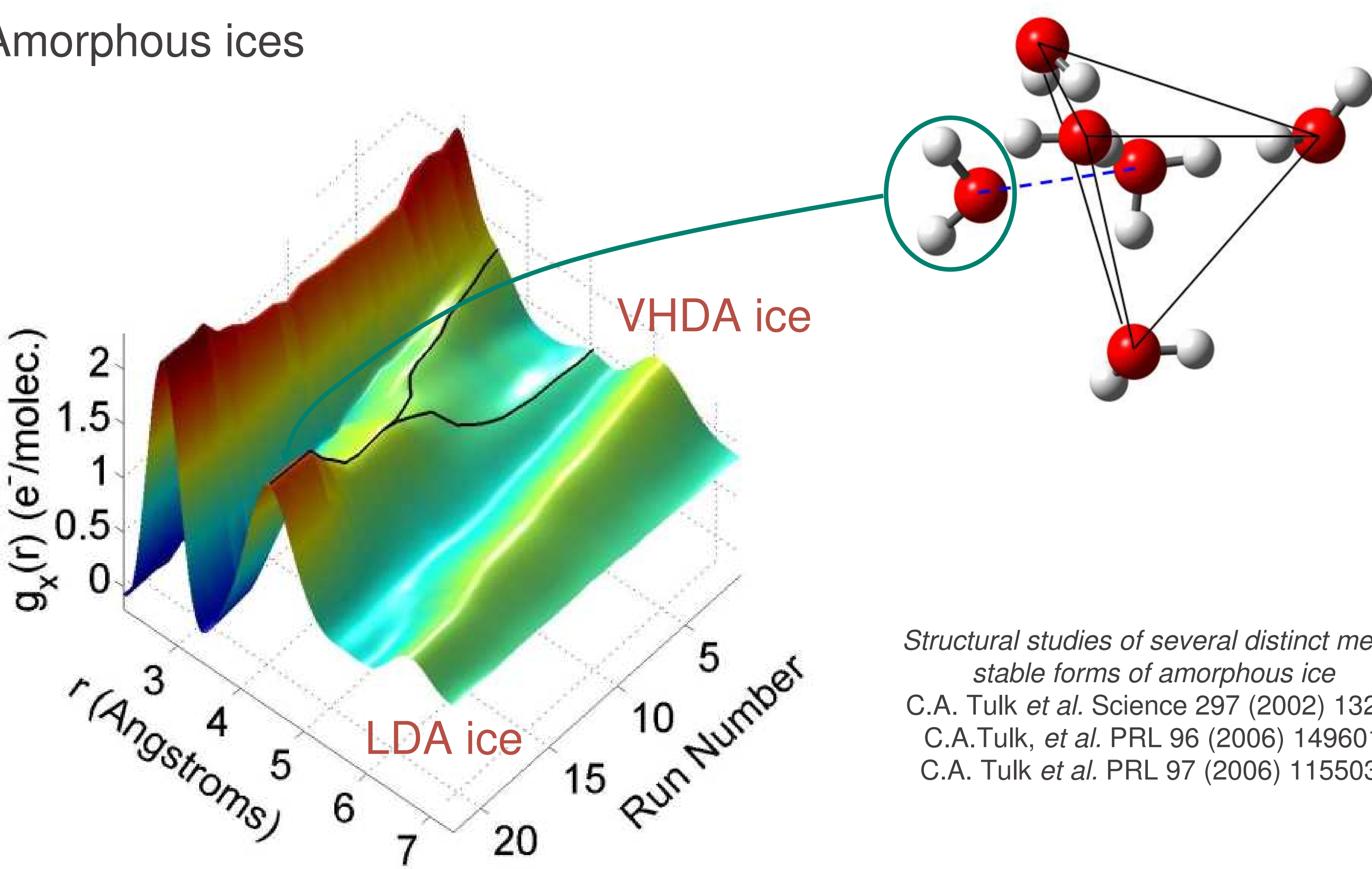



*The structure of alkali silicate gel by total scattering methods.*
C.J. Benmore and P.J.M. Monteiro. Cement and Concrete Research, submitted.

# *High Pressure*

- Amorphous ices

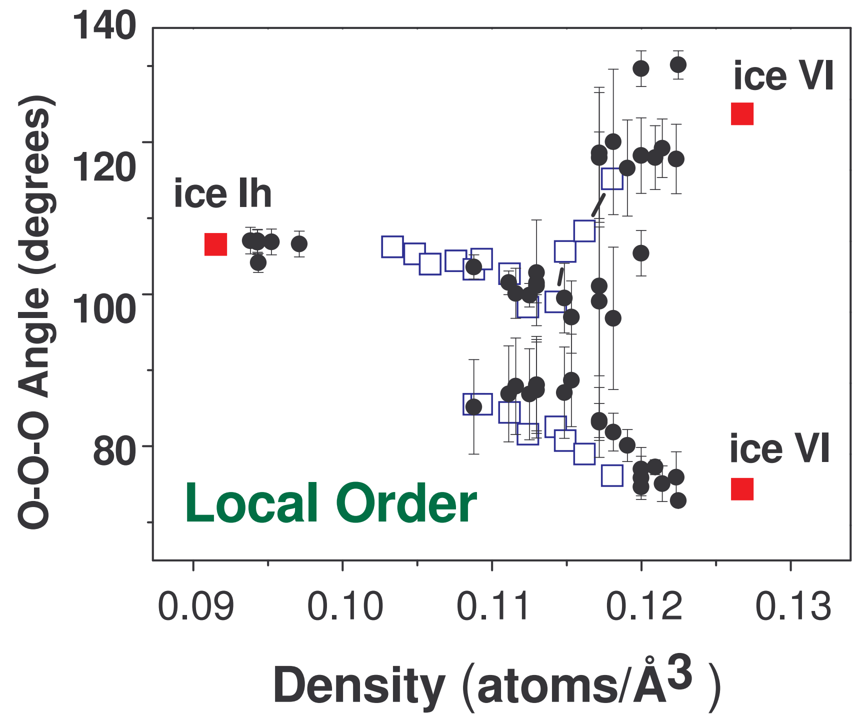



*Structural studies of several distinct meta-stable forms of amorphous ice*
C.A. Tulk *et al.* Science 297 (2002) 1320.
C.A.Tulk, *et al.* PRL 96 (2006) 149601.
C.A. Tulk *et al.* PRL 97 (2006) 115503.

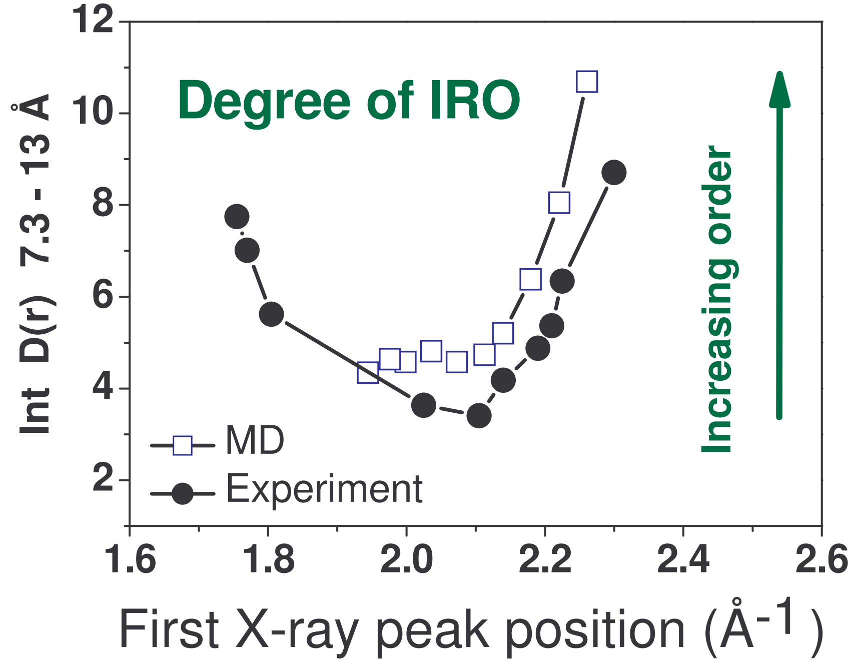
# *Local and intermediate order in amorphous ices*

LDA HDA VHDA

Coordination # : 4 5 6




Abrupt Short range order changes




Continuous changes in intermediate range order

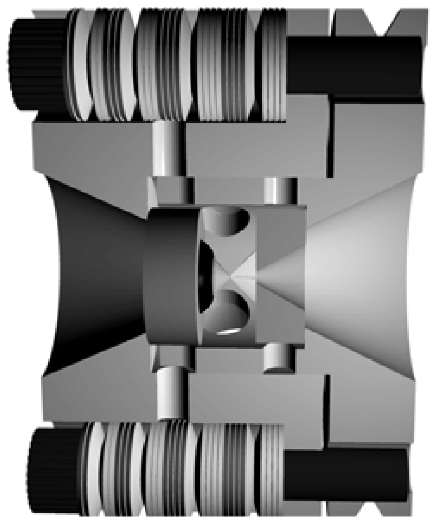
# *High pressure X-ray PDF on 1-ID*

Perforated diamonds

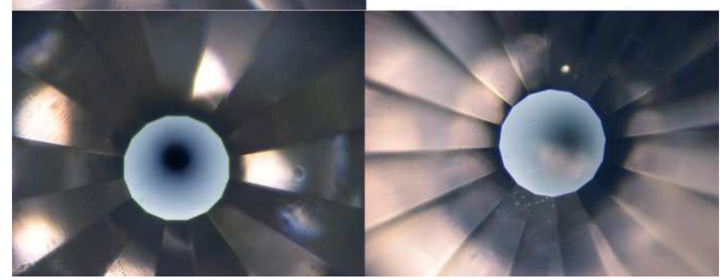
Pressure measurement :

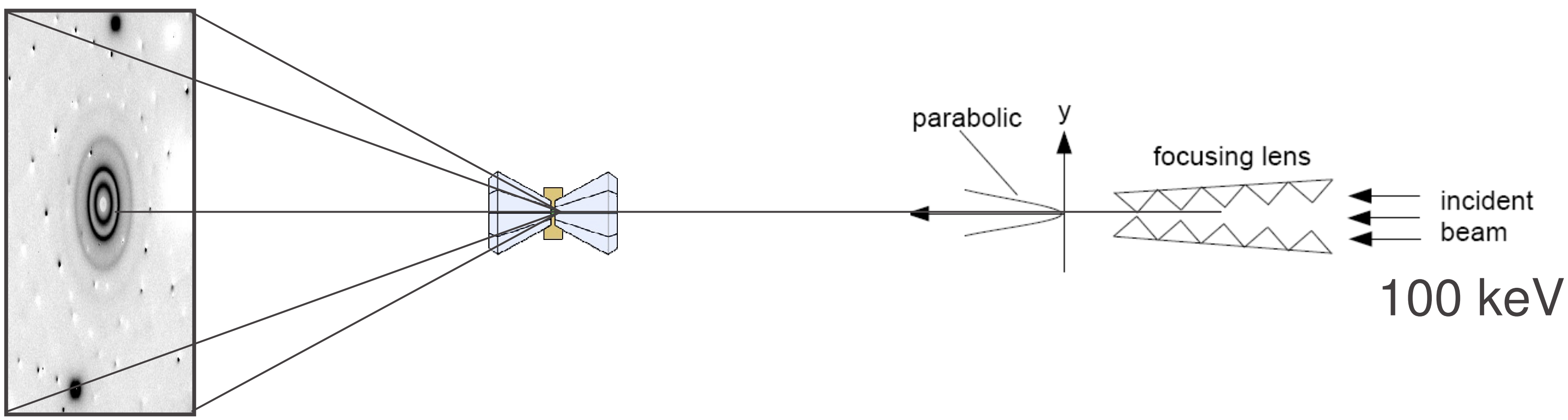
- Ruby Fluorescence
- Gold on inside of gasket

No pressure medium
(some tests with He)

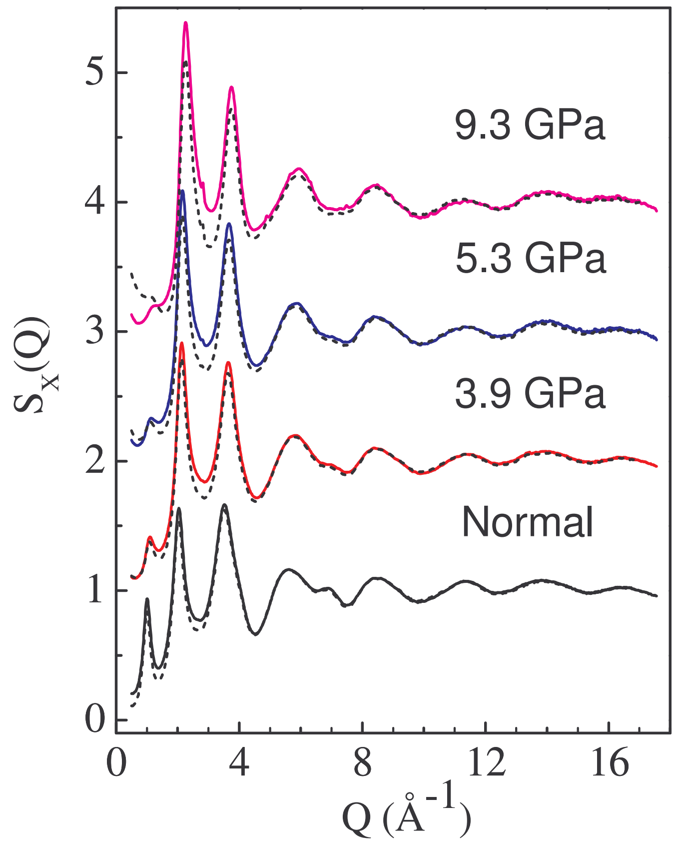


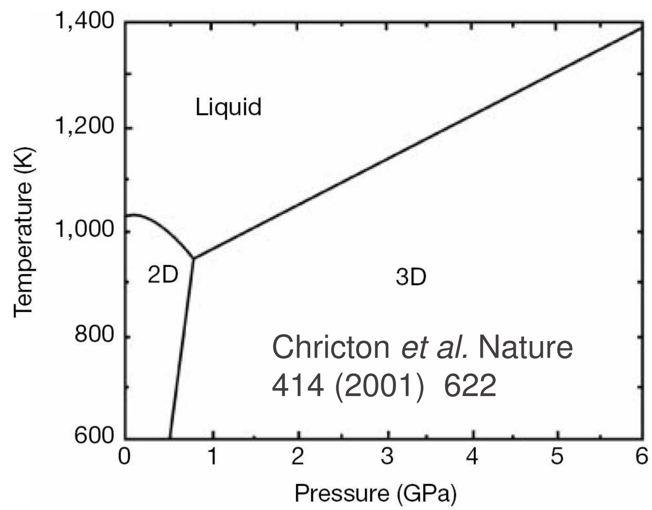
**Culet: 300 μm**
**Opening at culet: ~80 μm**
**Beam diameter: ~ 30 μm**





# *Breakdown of intermediate range order*

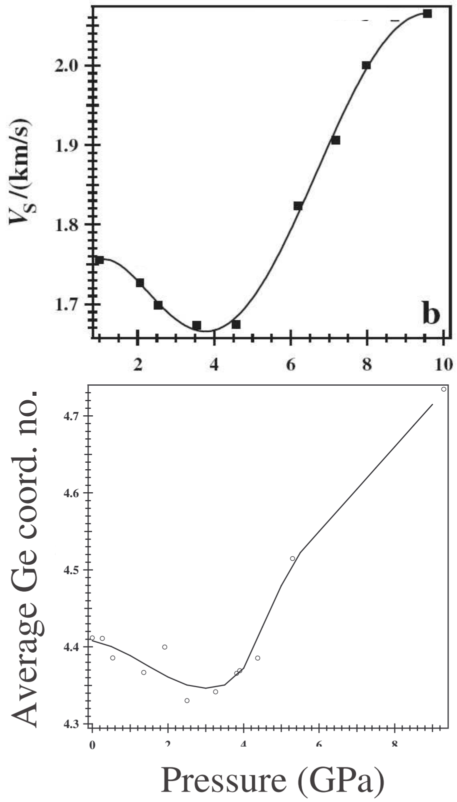


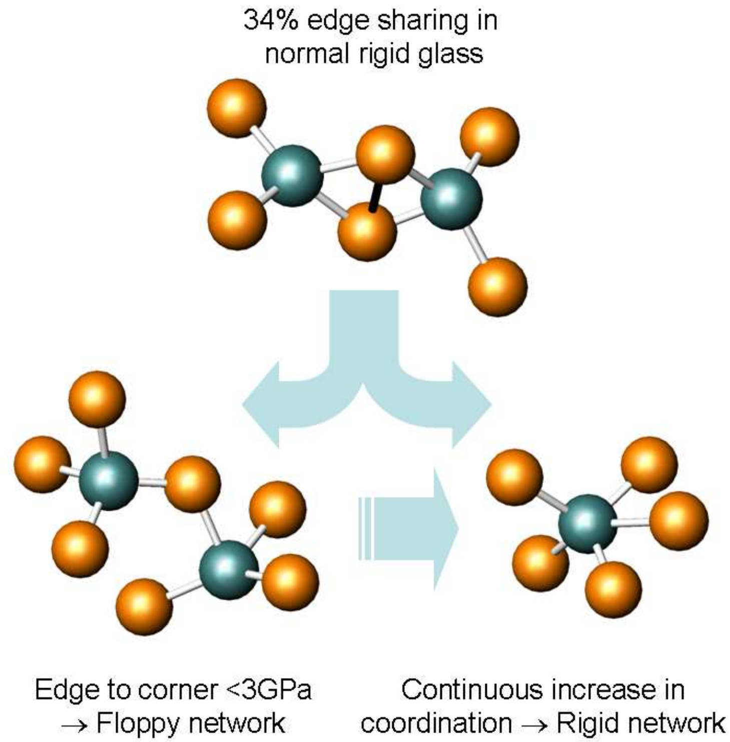

*Topological changes in glassy $GeSe_2$ at pressures up to 9.3GPa determined by high energy x-ray and neutron diffraction measurements.*
Q. Mei *et al.* PRB 74 (2006) 014203.

# *Two densification mechanisms*

Shear velocity at high pressure



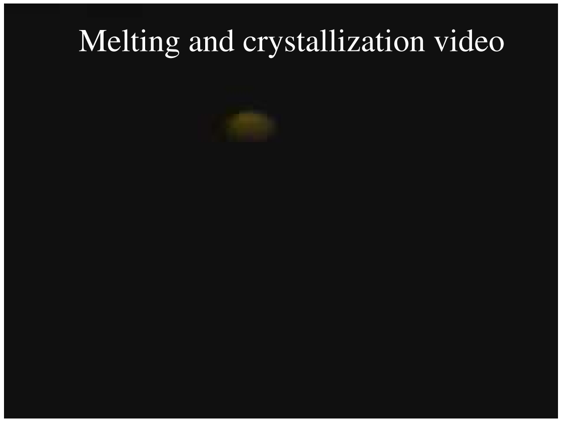

Sum of local coordination plus edge sharing contributions.




Formation of larger, more flexible ring structures.

*Network Rigidity in $GeSe_2$ glass at high pressure.*
S. M Antao, C.J. Benmore, L. Wang, B. Li, E. Bychkov, J.B. Parise.
PRL 100 (2008) 115501.

# *Aerodynamic levitation at 11-ID-C*

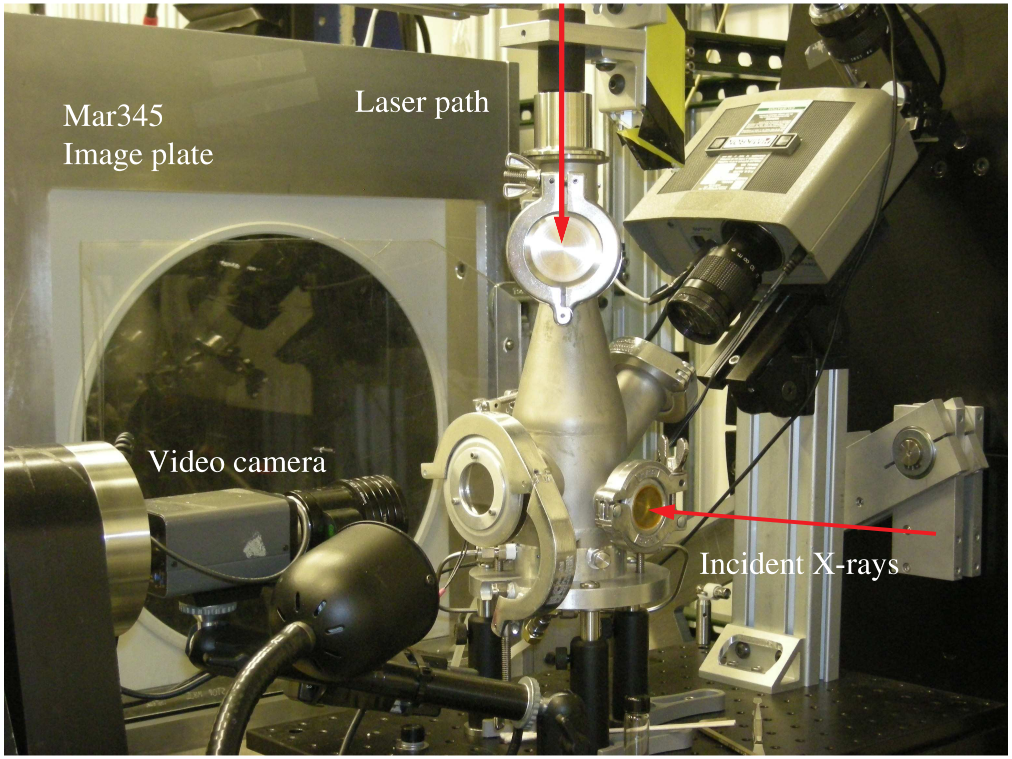




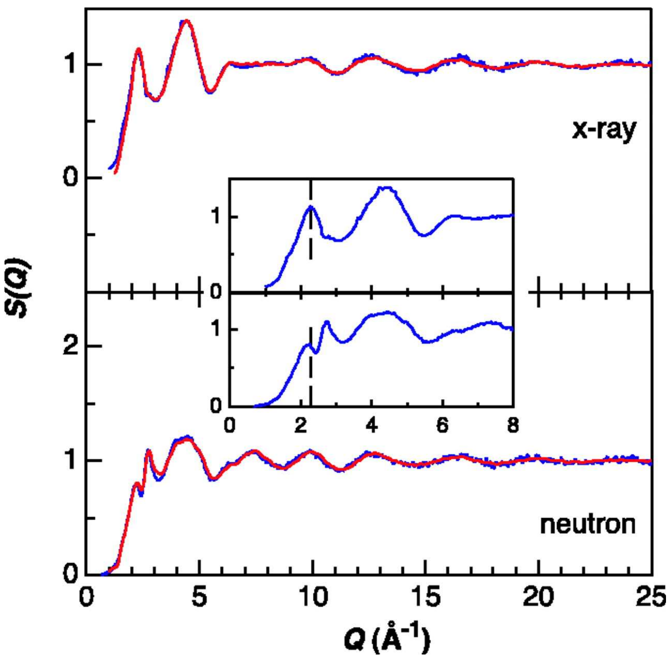
Laser heating & aerodynamic levitation with area detector.

Measurements of liquid structure can be made in minutes.

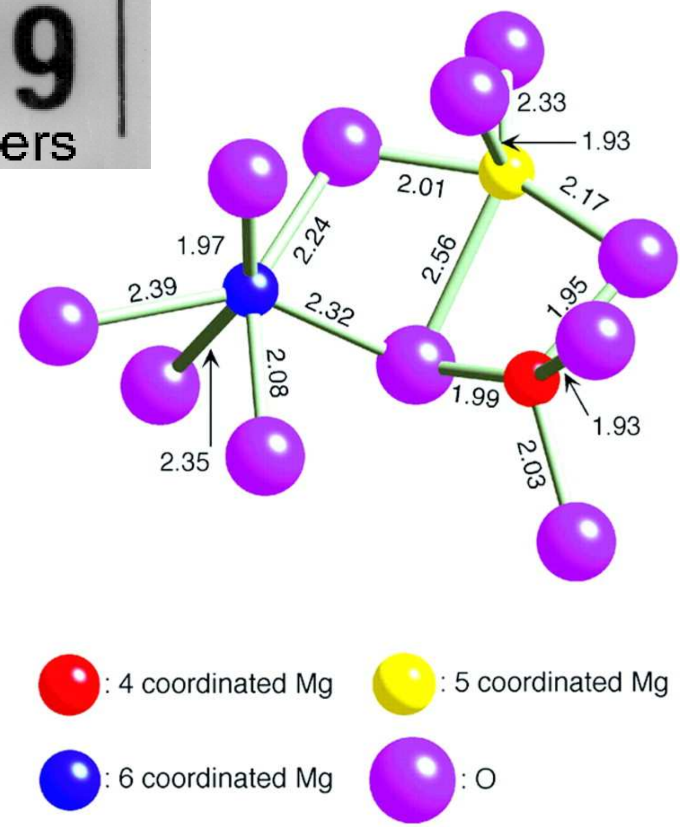
Liquid/glass structure at extreme temperatures from 1000 to 3000ºC.



# *Forsterite glass :$Mg_2SiO_4$*

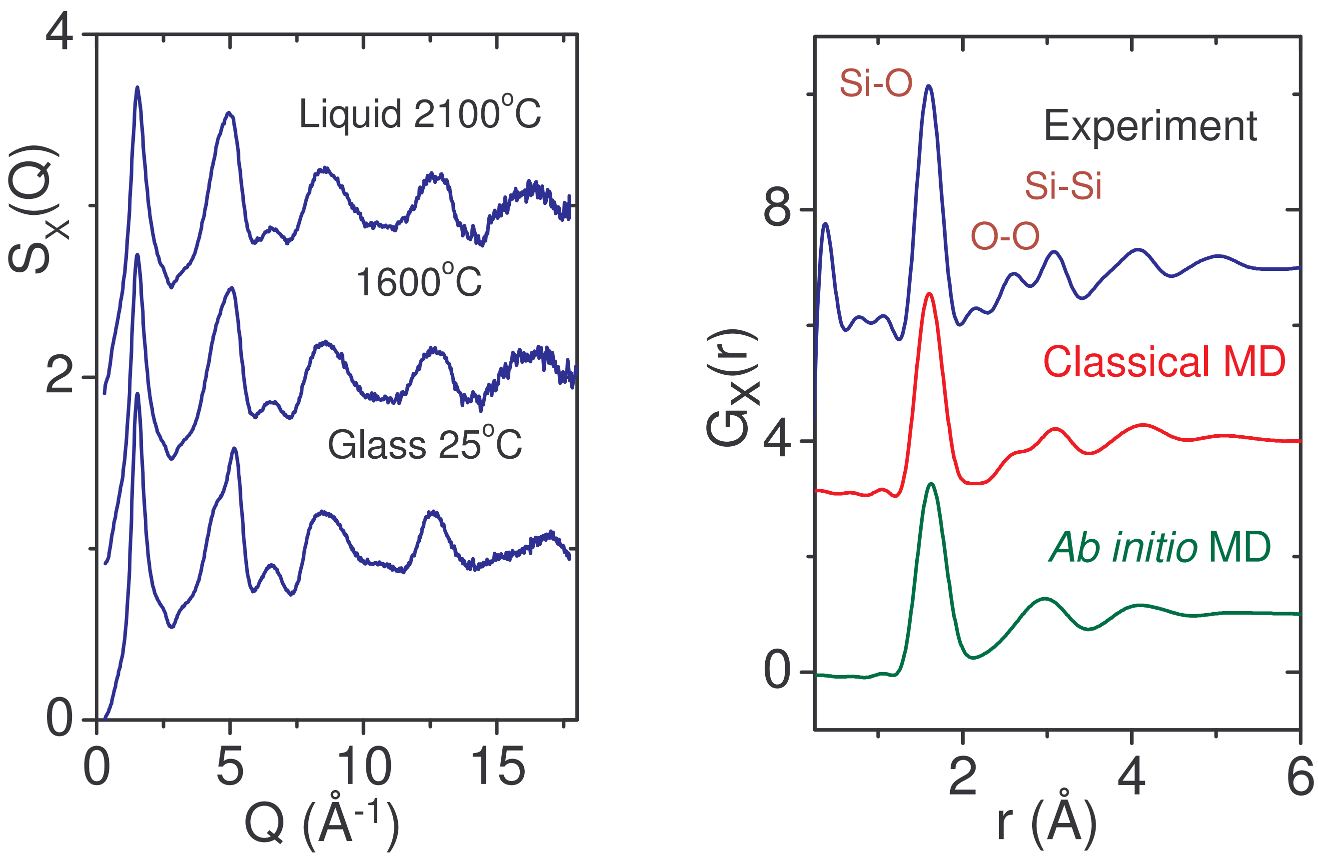







*Glass Formation at the Limit of Insufficient Network Formers*
S. Kohara *et al. Science 303 (2004) 1649.*

# *Liquid Silica*




*The structure of Liquid $SiO_2$*
Q. Mei, C.J. Benmore and J. Weber. PRL 98 (2007) 057802.

# *Outlook*

- Ability to quench glasses that do not normally vitrify using traditional methods :

  Containerless from high temperature

  Or, from a minimum in the melt line with pressure

Able to form new structures from existing materials

- Time resolved measurements through the glass transition.
- Study of hetrogeneous amorphous structures.

# *Collaborators*

Rick Weber, Qiang Mei, Rober Hart – Argonne National Laboratory

Jeffery Yarger, Emmanuel Soignard, Samrat Amin – Arizona State University

John Parise – Stonybrook University

Martin Wilding, Neville Greaves – University of Aberystwyth, UK.

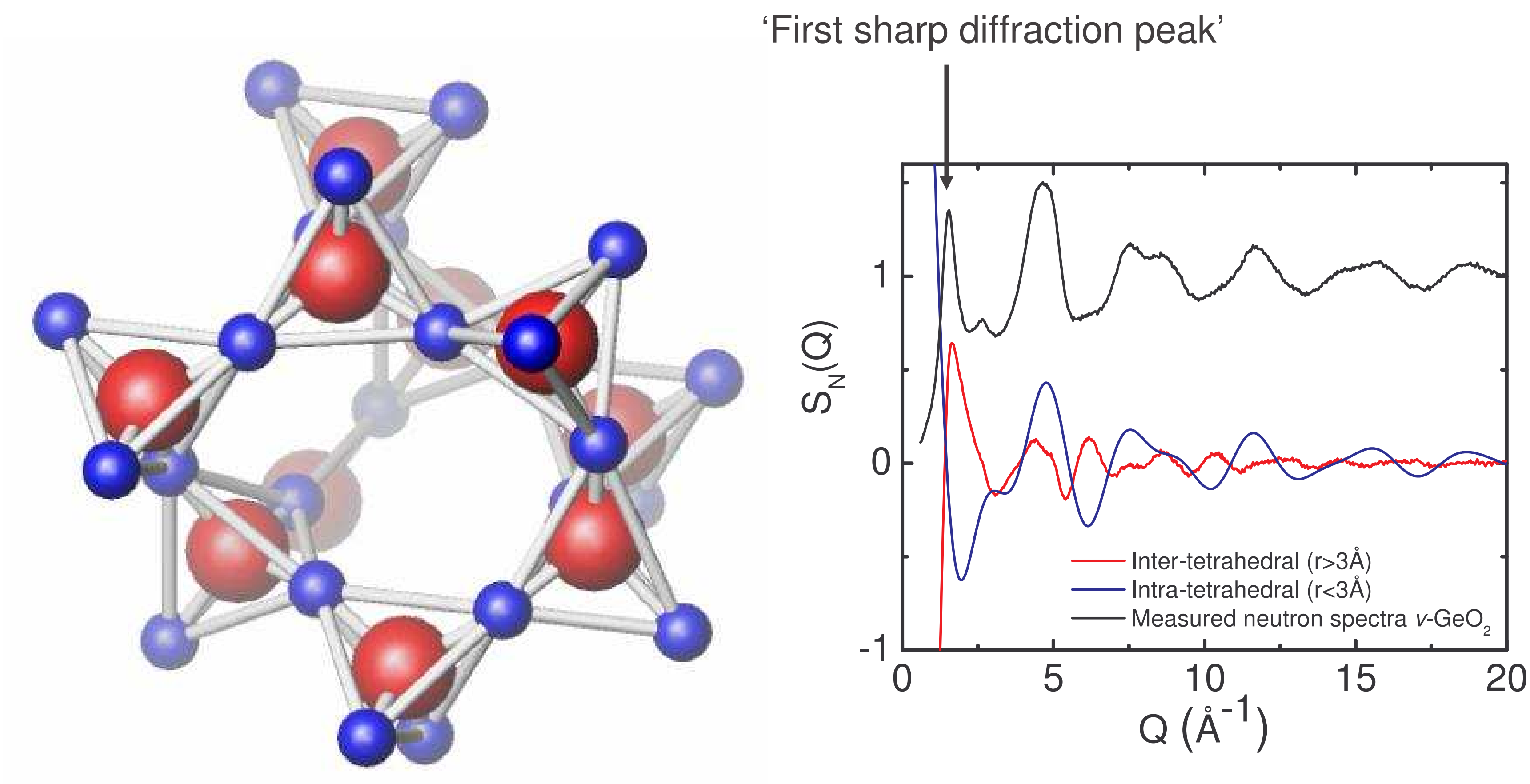
Sabyasachi Sen – University of California at Davis

Eugene Bychkov – University of Littoral, France

Shinji Kohara – Spring-8, Japan.

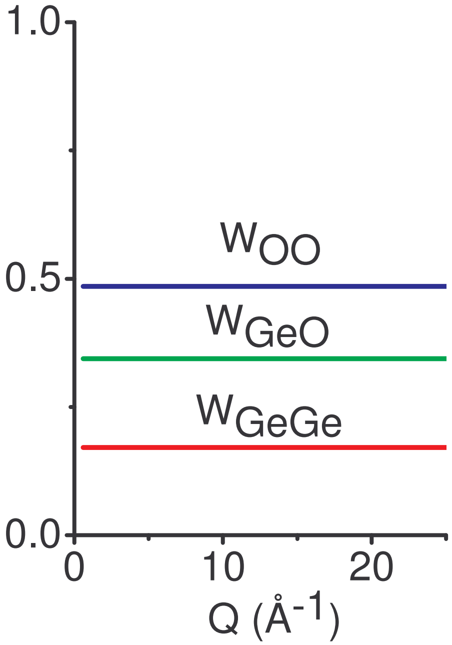
# *Additional slides*

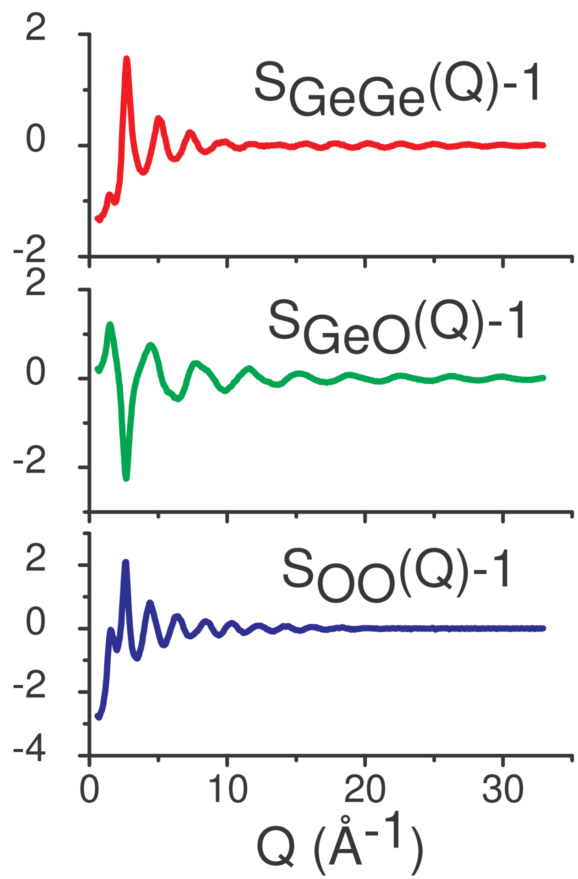
# Short and intermediate range order



# Neutrons vs. X-rays : The case of vitreous $GeO_2$

Neutron weighting factors, $W_{\alpha\beta}(Q)$




Partial Structure Factors, $S_{\alpha\beta(}Q)$

X-ray weighting factors, $W_{\alpha\beta}(Q)$